SURVEY OF HOMOGENEOUS

REACTOR CHEMICAL PROBLEMS

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CHEMICAL PROBLEMS

C. H. Secoy

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Abstract

This paper presents a survey of the principal chemical factors involved
in the selection of a fuel-bearing solute for use in an aqueous homogeneous
reactor and of the chemical phenomena encountered in the operation of such a
reactor. Phase diagrams for systems involving uranyl nitrate, fluoride, phos-
phate, chromate and sulfate are presented and discussed. The effects of reactor
radiation on the solute and the solvent in each case are discussed and an
appraisal of the limitations placed on reactor operation by chemical factors
is presented. In particular, the kinetics of the peroxide problem are given
in detail.

SURVEY OF HOMOGENEOUS REACTOR

CHEMICAL PROBLEMS

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During the course of the development of the Homogeneous Reactor Project
at Oak Ridge National Laboratory an extensive and vigorous research program
dealing with the chemical problems of a water moderated homogeneous reactor
was pursued. This paper presents a survey of some of the significant results
of these researches. In many instances the research was exploratory only but
was adequate to indicate general comparative feasibility. In other instances
carefully performed, quantitative experiments were required in order for the
results to be of any significance.

The initial problem was the selection of a fuel system with which one
could be reasonably certain of satisfactory performance and which would minimize the probability of encountering operational difficulty. Therefore, it
was necessary to understand and delineate the chemical phenomena which could
occur in a homogeneous aqueous fuel system in order either to anticipate and
avoid operational trouble or to correct it if it occurred.

The obvious general requirement is that the fuel system retain its homogeneity, especially with respect to the uranium fuel atoms, under all operating
conditions. Picture, if you will, an n-dimensional space of homogeneity with
dimensions for the concentration of each component of the system, for temperature, for pressure, and for each radiation type, intensity, and energy. The
boundaries of this space are n-1 dimensional "surfaces" of non-homogeneity.
One must find a system capable of existence within this space as determined by

reasonable values of the parameters. These are fixed by the selected speci-
fications of the reactor and the purpose for which it is intended. Furthermore,
the point of normal operation within the space must be sufficiently distant
from any of the boundary surfaces to allow considerable variation in conditions
because of the practical limitations on the control of the reactor system.

Aside from this generality, the components of the system must be selected
with neutron economy in mind. For the barest minimum the system must be capable
of achieving criticality and, for economical operation, the maximum utilization
of the available neutrons is a prime objective. Therefore components contain-
ing only atoms of reasonably low neutron capture cross sections may be used.

Finally, the system must be sufficiently non-corrosive to some otherwise
acceptable container material to insure a reasonably long and safe life-time
for the reactor.

Early experiments involving the exposure of uranium salt solutions to the
radiation of the Oak Ridge graphite reactor established the fact that hexavalent
uranium was the stable oxidation state. Therefore, the program concerned it-
self with only uranyl compounds. The specific salts which will be discussed
include uranyl nitrate, uranyl phosphate, uranyl chromate, uranyl fluoride, and
uranyl sulfate. In the case of each of these, aqueous solutions of the stoi-
chiometrically neutral salts are acidic because of hydrolysis. An increase of
temperature promotes the hydrolysis reaction without exception and thus, one
may obtain at elevated temperatures an acid-rich liquid phase and a basic or
basic-salt solid phase from solutions which would otherwise be far from saturated.
For this reason it is necessary to consider each as a three-component system,
the components of which may be taken as UO_3, the respective acid anhydride,
and water.

The data resulting from a study of the solubility of uranyl nitrate in water as a function of temperature are shown graphically in Figure 1.[6] The significance of the data is simply that the solubility far exceeds that required for a reactor at all temperatures up to the congruent melting point of the dihydrate at 184°C. However, as shown in Figure 2, at higher temperatures stoichiometric solutions of all concentrations undergo thermal decomposition of the nitrate ion and hydrolytic precipitation of a basic salt. If operation of a reactor at such temperatures was to be considered, the hydrolytic precipitation could be avoided by enriching the solution with nitric acid. The loss of oxides of nitrogen in the vapor phase would have to be compensated for by appropriate additions of acid. Under reactor radiation and in the presence of fission-recoil particles, uranyl nitrate solutions show an additional instability. Nitrogen gas as well as nitric oxide is produced even at lower temperatures.

The compound uranyl orthophosphate is insufficiently soluble in water to be of interest. At elevated temperatures such systems disproportionate into an acid-rich solution in equilibrium with a basic salt. Thus by increasing the ratio of phosphate ion to uranyl ion, solutions stable to as high as 500°C and with adequate uranium content can be obtained. Such high phosphorus-to-uranium ratios detract from neutron economy and, probably more serious, the solutions are extremely corrosive to most of the desirable container metals and alloys. The phosphate ion has been shown to be adequately stable to reactor radiation.

The solubility of uranyl chromate as a function of temperature is shown graphically in Figure 3.[5] The solubility increases rapidly from 25° to 66.3°C but is nearly invariant at higher temperatures. Here again, even though the
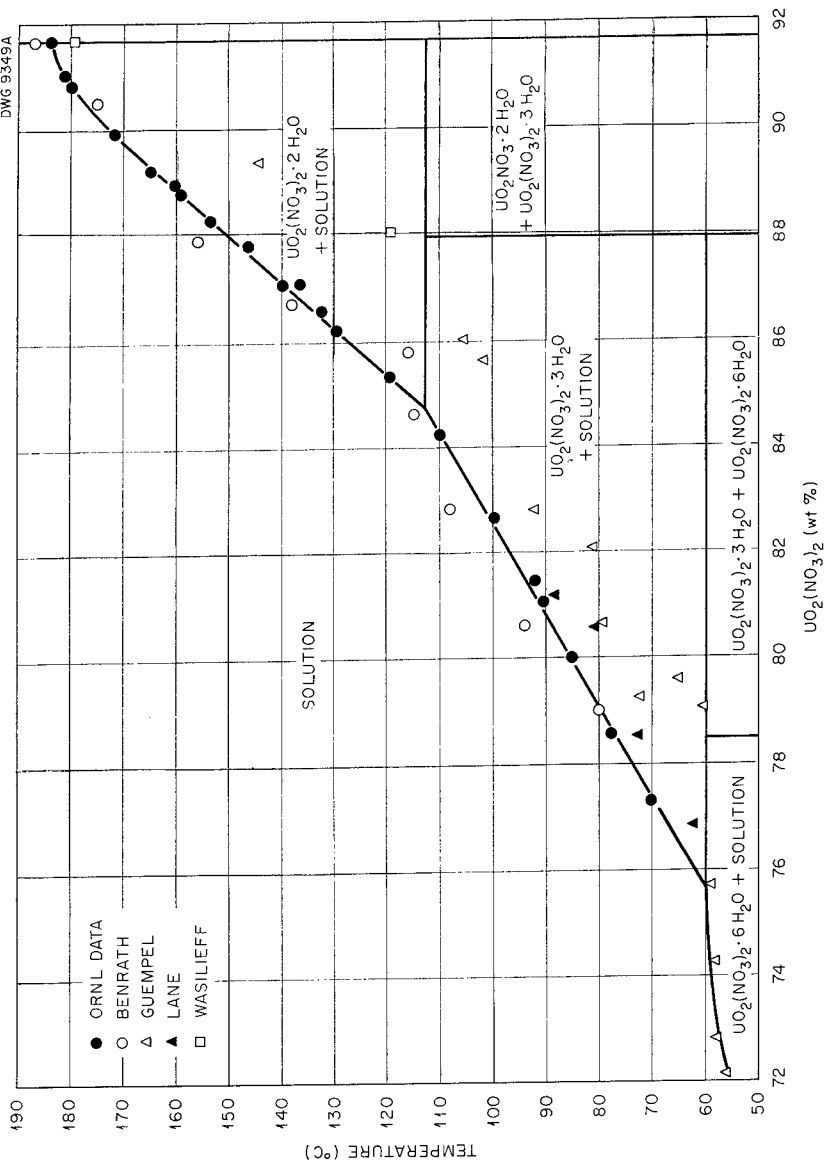
Fig. 1. The Solubility of $UO_2(NO_3)_2$ in H_2O
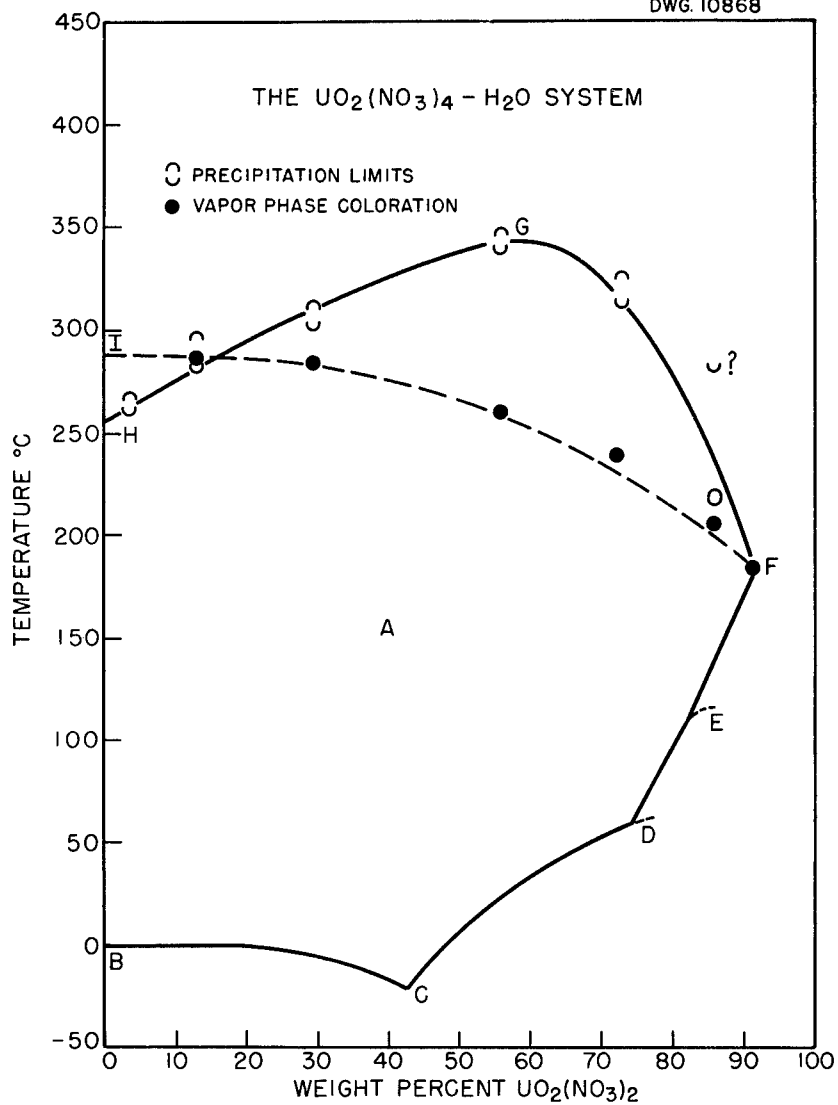
Fig. 2. Thermal Stability of Uranyl Nitrate Solutions.
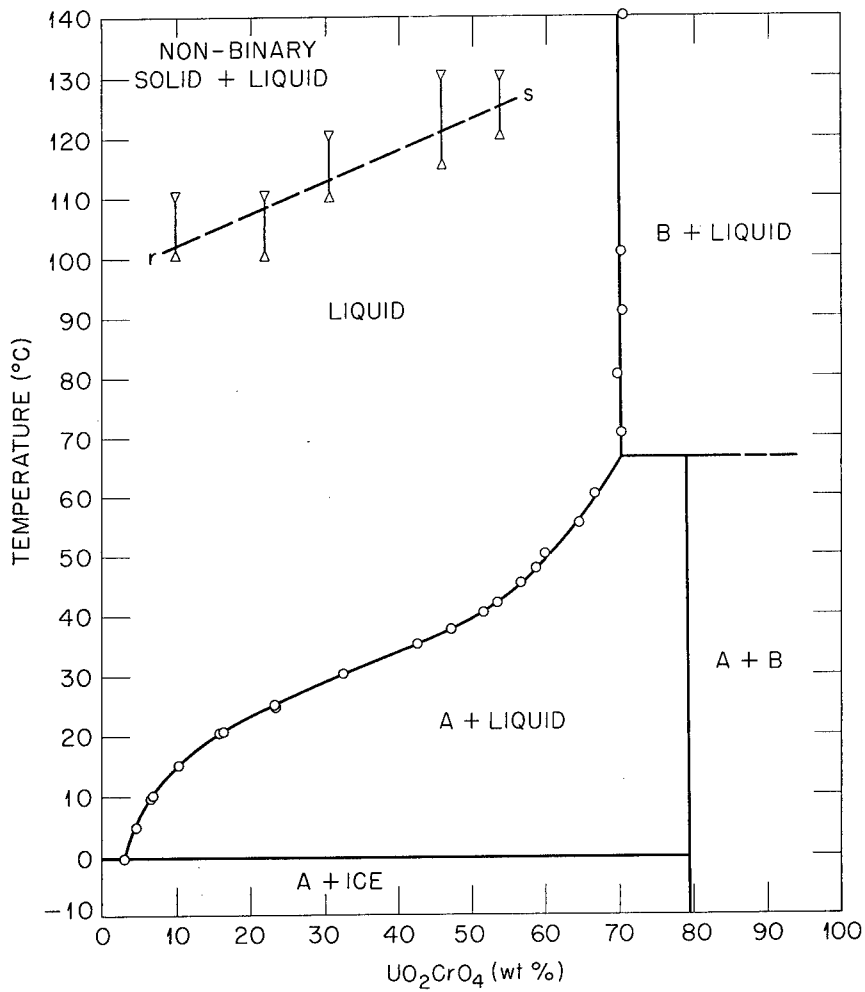
Fig. 3. The System UO₂CrO₄-H₂O.

solubility is adequate to be of interest, hydrolytic precipitation of a basic salt occurs as shown by the non-binary solid-liquid line in the diagram. Further experimentation has shown that this phenomenon may be easily avoided by the addition of excess chromic acid anhydride. In fact properly selected compositions undergo critical transformation without the appearance of a solid phase, the solute including the uranium being soluble in the supercritical fluid. However, reactor radiation has been shown to reduce hexavalent chromium to trivalent in solutions of a pH of 3 or less and the trivalent chromium is precipitated hydrolytically. Thus, for high temperature reactors, insufficient stability space appears available for safe, trouble-free operation. Further research may disclose a way around this difficulty. In so far as corrosion is concerned a few exploratory experiments have indicated that a chromate system contained in some of the ordinary steels might be superior among those discussed here.

Uranyl fluoride is a highly soluble compound and its aqueous solutions are very attractive in so far as radiolytic stability and neutron economy are concerned. However, at elevated temperatures a different and interesting phenomenon occurs. This is the appearance of a two-liquid phase region or miscibility gap. The solubility data are shown in Figure 4.[7] Region K in the Figure represents unsaturated solution for the system. Line A B C D E is the uranyl fluoride solubility curve, transitions occurring in the solid phase at C and at D. The invariant point temperature along GE (333°) was fixed by liquefaction upon lowering the temperature of the solid $(\gamma UO_2F_2 \cdot 2H_2O)$ which is stable above line GE. The region immediately above FE represents a two-liquid phase region. The minimum of the curve is not consolute in that the two phases involved at that point are not identical. The consolute temperature
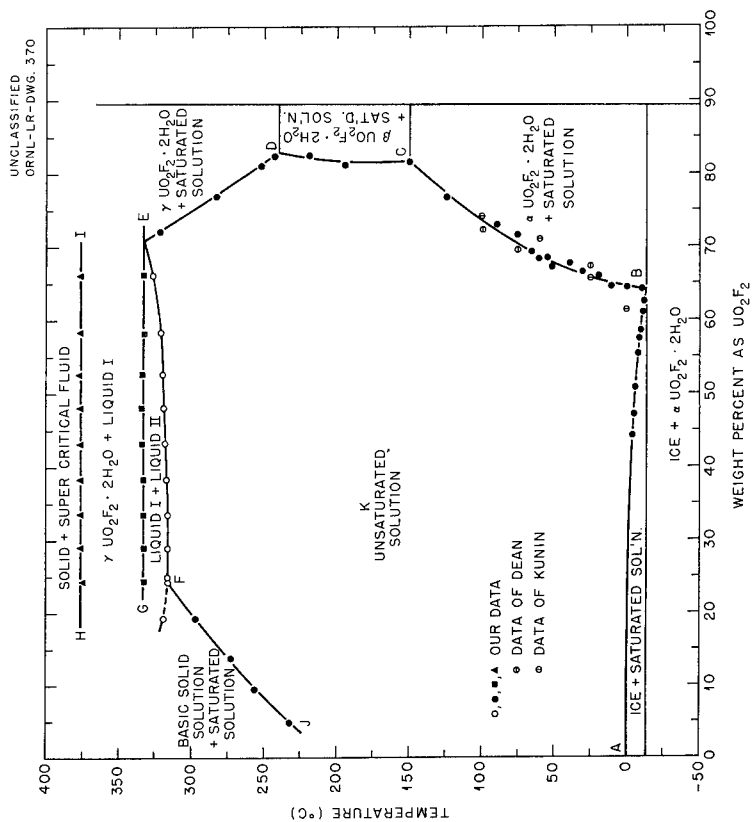
Fig. 4. Phase Equilibria of UO_3 and HF in Stoichiometric Concentrations.

for the diagram occurs between 48.7 and 52.75% UO_2F_2. On the left of this point in the figure the UO_3 rich phase appears as a second liquid upon raising the temperature while on the right the new phase is the water rich liquid. This fact constitutes evidence that the system is ternary and must be so depicted for complete understanding.

Solutions more dilute than approximately 25% UO_2F_2 yield a solid phase at temperatures indicated by line JF, well below the two-liquid phase region. This solid has been shown to be a solid solution of $UO_2(OH)_2$ and either $UO_2(OH)F \cdot 1/2H_2O$ or $UO_2F_2 \cdot H_2O$. Here, as in the previous cases, the hydrolytic instability can be prevented by enriching the system with the acidic component, HF. The only serious objection to the utilization of the fluoride system for high temperature reactor purposes is the expectation that corrosion rates would be prohibitively high. This expectation has been partially confirmed by experiment.

Uranyl sulfate is also a very soluble compound and one which has been shown to be completely stable under reactor radiation when in aqueous solution. The phase equilibria in the binary system, uranyl sulfate-water, are shown in Figure 5.[8,9] The solubility of the stoichiometric salt remains far greater than required for a reactor fuel at all temperatures up to at least 400°C. A two-liquid phase region of somewhat greater scope than in the case of uranyl fluoride appears with solutions unsaturated with respect to the stoichiometric salt. The upper temperature limit of the two-liquid phase region is the critical temperature of the water rich phase, 374° ± 1.0°C. As in the case of uranyl fluoride the minimum temperature for the region is not consolute since the two phases are not identical. This established the fact that the region is ternary.
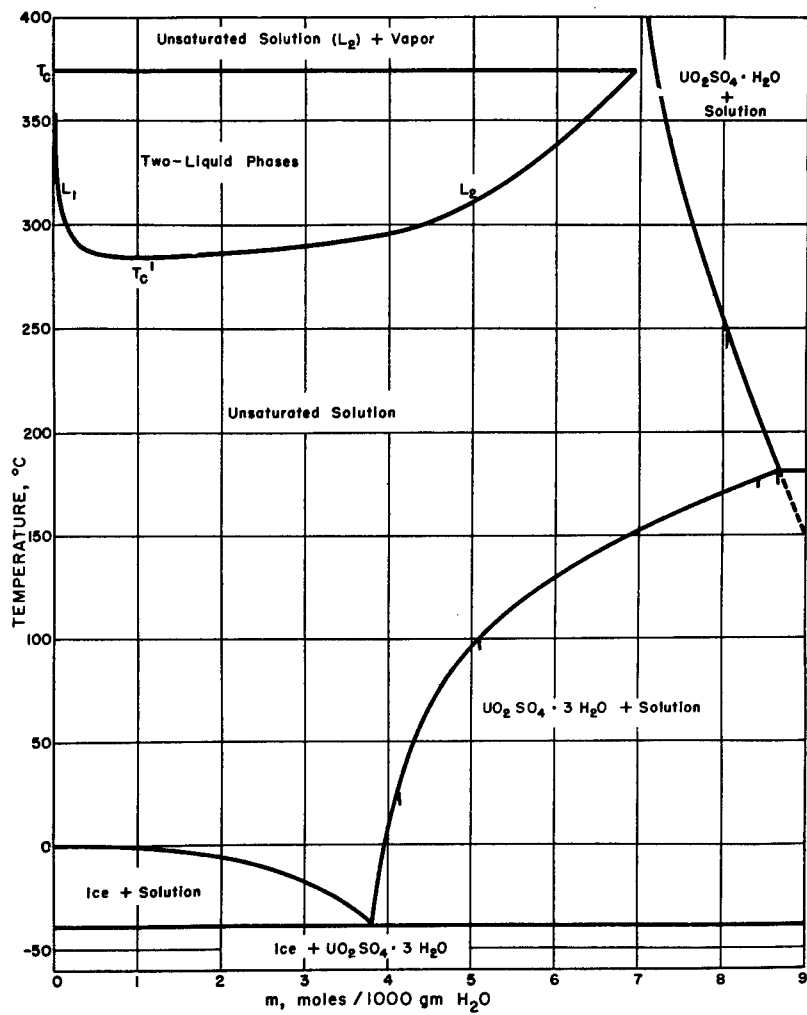
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Unsaturated Solution (L₂) + Vapor

T_c

Two-Liquid Phases

L_1

T_c'

L_2

$UO_2SO_4 \cdot H_2O$
+
Solution

Unsaturated Solution

$UO_2 SO_4 \cdot 3 H_2O$ + Solution

Ice + Solution

Ice + $UO_2 SO_4 \cdot 3 H_2O$

TEMPERATURE, °C

m, moles / 1000 gm H₂O

Fig. 5.   Phase Diagram for the System Uranyl Sulfate-Water.

Studies of portions of the ternary system, UO_3-SO_3-H_2O have been made at 25, 100, 175, and 250°. Diagrams for these isotherms are shown in Figures 6 to 9, respectively. The data on the SO_3 rich portion of Figure 6 were calculated from work by Colani.[4] It is evident from Figure 6 that solutions with uranium concentrations in the range of general reactor interest are most endangered by the nearness of the UO_3 rich solubility curve. In fact as temperature is increased this curve moves to the left and, at 250°, stoichiometric solutions of low concentration disproportionate into an acid rich solution and a precipitate of $UO_3 \cdot H_2O$. If such solutions are to be used in a reactor at high temperatures the addition of sulfuric acid is necessary to maintain homogeneity. The introduction of corrosion products and fission products which contribute to the basicity of the system must also be compensated by the presence of excess acid.

Studies of the ternary system at higher temperatures at which the two-liquid phase separation may occur have not progressed sufficiently for a quantitative and complete picture to be presented. However a probably correct schematic understanding is possible. Figure 10 presents data illustrating the effect of excess sulfuric acid on the temperature of appearance of the second liquid phase. From these curves one sees that as the sulfate to uranium mole ratio is increased the scope of the miscibility gap shrinks and the region moves to higher temperatures. Thus it is possible to avoid the region completely by making the solution sufficiently rich in sulfuric acid. Points may be selected from the curves of Figure 10 for the construction of isotherms in the ternary system. However, for a complete elucidation of this region, consideration of the composition of the vapor phase and of the effect of pressure is required.
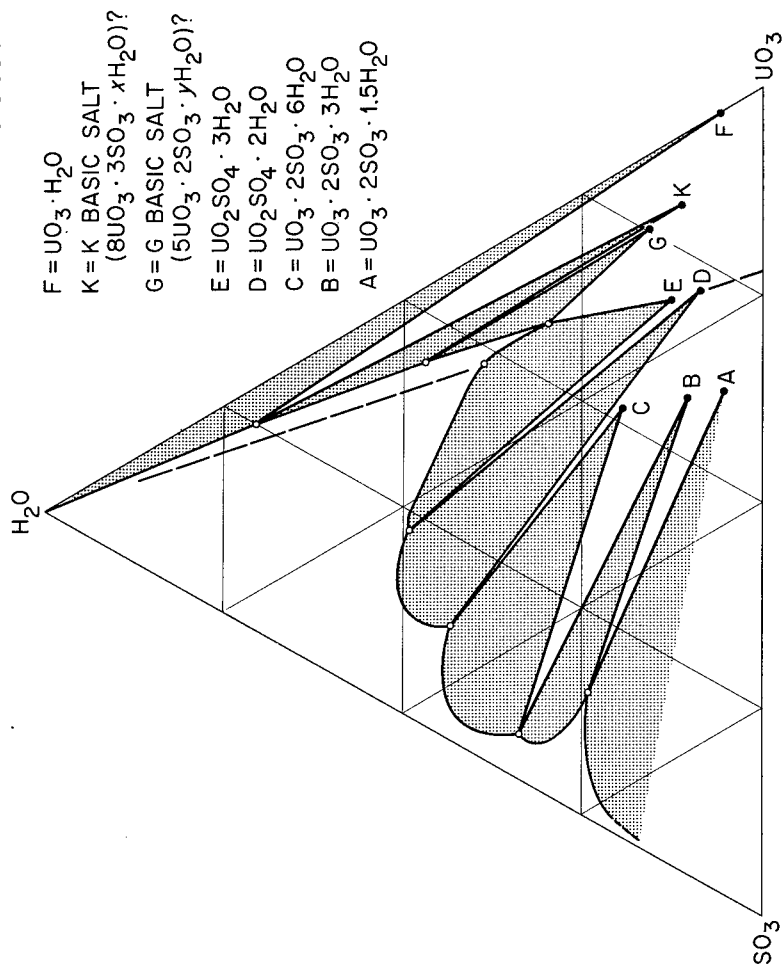
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F = $UO_3 \cdot H_2O$
K = K BASIC SALT
    $(8UO_3 \cdot 3SO_3 \cdot xH_2O)$?
G = G BASIC SALT
    $(5UO_3 \cdot 2SO_3 \cdot yH_2O)$?
E = $UO_2SO_4 \cdot 3H_2O$
D = $UO_2SO_4 \cdot 2H_2O$
C = $UO_3 \cdot 2SO_3 \cdot 6H_2O$
B = $UO_3 \cdot 2SO_3 \cdot 3H_2O$
A = $UO_3 \cdot 2SO_3 \cdot 1.5H_2O$

H_2O

UO_3

SO_3

Fig. 6. The System UO_3-SO_3-H_2O at 25°C.
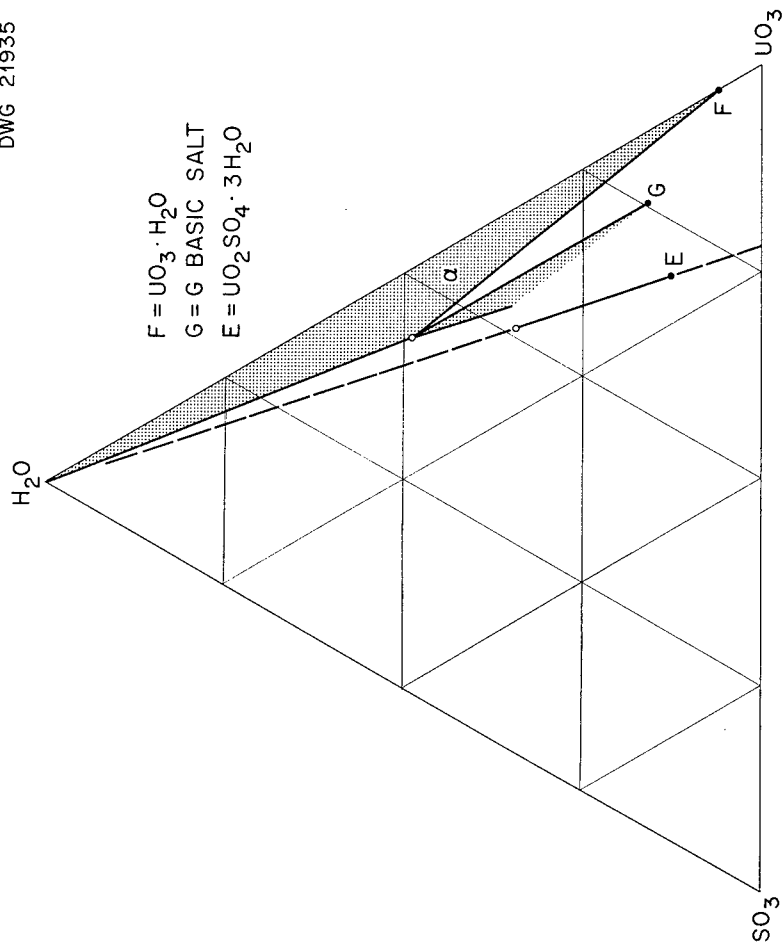
Fig. 7. The System UO_3-SO_3-H_2O at $100°C$.

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$F = UO_3 \cdot H_2O$

$G = G$ BASIC SALT

$E = UO_2SO_4 \cdot 3H_2O$
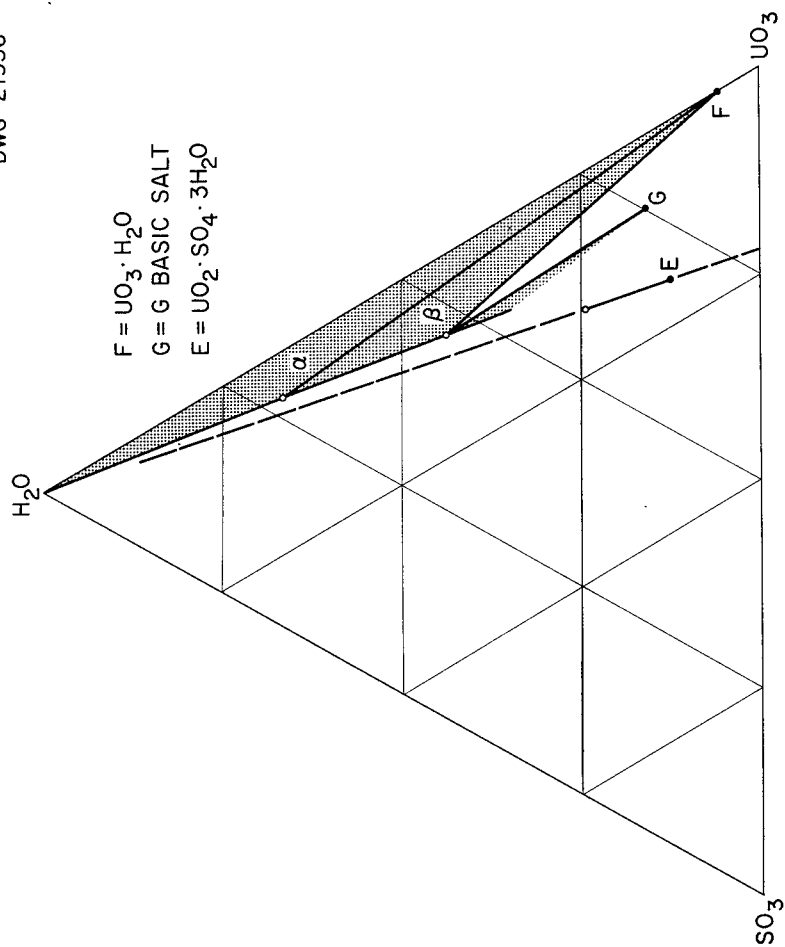
Fig. 8. The System UO_3-SO_3-H_2O at 175°C.

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$F = UO_3 \cdot H_2O$
$G = G$ BASIC SALT
$E = UO_2 \cdot SO_4 \cdot 3H_2O$

H_2O

UO_3

SO_3

α

β

E

G

F

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SOLID PHASE : $\beta\ UO_3 \cdot H_2O$

H₂O

UO₃

0.25

0.75

0.50

0.50

0.75

0.25

SO₃

99.75

99.50

99.25

CROSS OVER

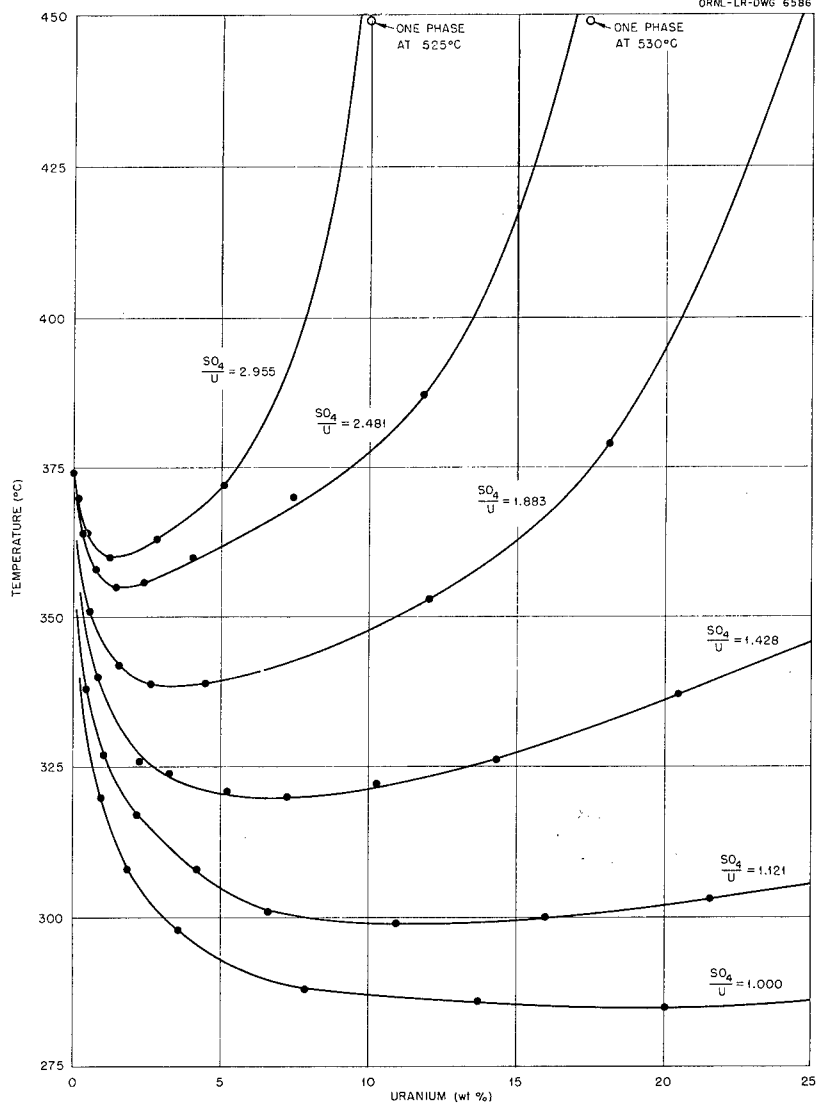Fig. 9. The System $UO_3\text{-}SO_3\text{-}H_2O$ at 250°C.
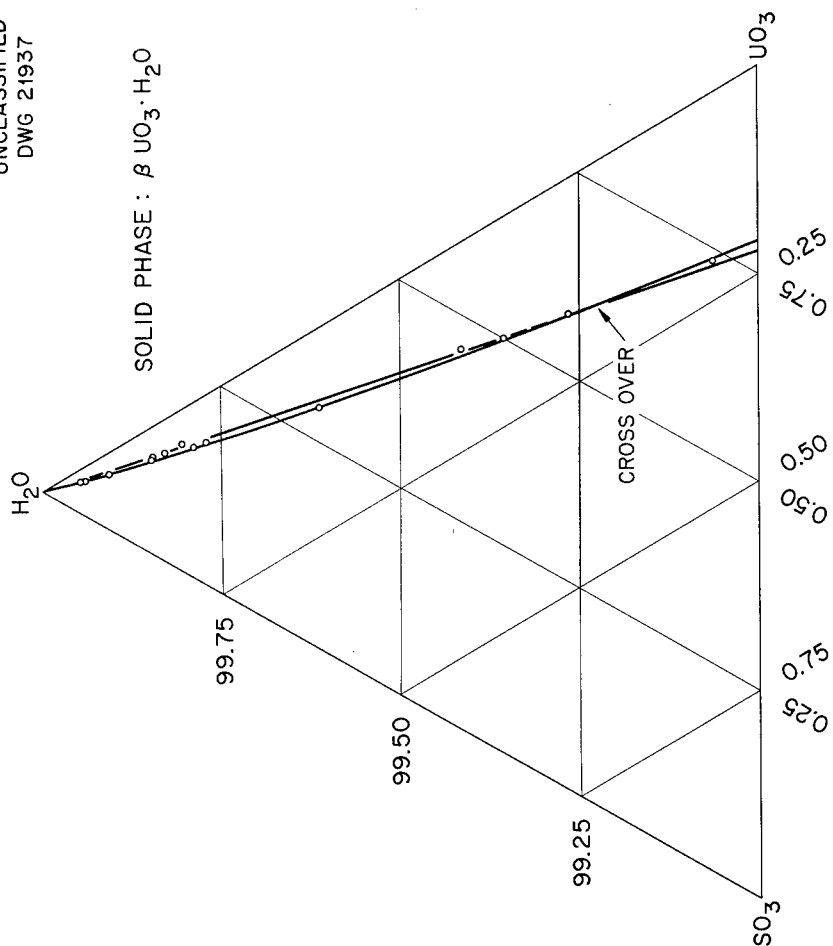
Fig. 10. Coexistence Curves for two Liquid Phases in the System UO_2SO_4-H_2SO_4-H_2O.

Finally, we have remaining a consideration of the effects of reactor
radiation on the solvent, water. The decomposition of water by fission recoil
particles has been studied by several people[1] and the principal observations
of concern are as follows. The primary products of the fission fragment im-
pact are the free radicals, H and OH. These may react with each other in the
fission track to produce H_2O, H_2, or H_2O_2. Therefore, the products of the
forward reaction may be regarded as hydrogen molecules and hydrogen peroxide.
On the other hand, the free radicals, H and OH may escape from the fission track
without interaction to react later with water molecules or other species present.
These latter processes detract from the efficiency of the hydrogen and hydrogen
peroxide production and, furthermore, give rise to high potentiality for the
occurrence of either oxidation or reduction reactions involving the solute.
For this reason ionic species capable of existence in more than one valence
state are in a delicate and precarious balance in irradiated aqueous systems.
This point has been illustrated by previous comments on the stability of hexa-
valent chromium and the observation that irradiated nitrate solutions yield
nitrogen gas.

Returning to a consideration of the effects of the ultimate products of
the radiolytic decomposition of water, the yields of hydrogen gas and hydrogen
peroxide have been determined in several uranyl salt solutions and have been
reported in detail at the United Nations Conference on Peaceful Uses of Atomic
Energy at Geneva.[3] Suffice it to say here that the yields expressed in mole-
cules per hundred electron volts of absorbed energy are essentially constant
with temperature and vary only slightly for different uranyl salt solutions and
for different uranium concentrations in moderately dilute solutions. For our
purpose the yield of either hydrogen or hydrogen peroxide may be considered
constant and equal to about 1.5 molecules per 100 electron volts.

Hydrogen peroxide may thermally decompose to form water and oxygen gas, or it may react with uranyl ion according to the equation,

$$UO_2^{++} + H_2O_2 = UO_4(aq) + 2H^+ \quad \text{---------------} \quad (1)$$
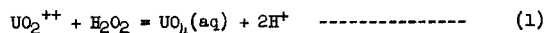
The UO_4, being rather insoluble, may precipitate as $UO_4 \cdot 2H_2O$ if its solubility is exceeded or it may also thermally decompose according to equations (2) and (3).

$$UO_4 = UO_3 + 1/2 \ O_2 \quad \text{------------------} \quad (2)$$

$$UO_3 + 2H^+ = UO_2^{++} + H_2O \quad \text{------------------} \quad (3)$$
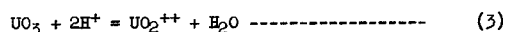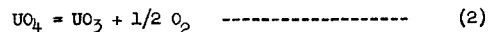
Studies of the kinetics of the decomposition of peroxide in uranyl sulfate solutions have shown the rate to be first order with respect to the peroxide concentration, independent of the uranium concentration and, within limits, independent of the acidity of the solution. These studies were carried out by adding an amount of hydrogen peroxide, insufficient to precipitate uranium peroxide, to uranyl sulfate solutions and following the peroxide concentration with time. The reaction rates were determined at 53, 78, and 100°C for a variety of solutions. Figure 11 illustrates the data. The straight lines on the plot of logarithm of the peroxide concentration against time establishes the first order dependence. Figure 12 shows the temperature dependence of the specific reaction rates for three different uranyl sulfate solutions. The slope of the lines indicates an activation energy of about 25.5 kilocalories. The fact that the three solutions gave different rate constants is attributed to differences in purity of the solutions. The pronounced catalytic effect of traces of certain ions on the decomposition of peroxide has long been known.[2] In order to test this hypothesis the effect of added ferrous ion was determined, the results being shown in Figure 13. The presence of only a few parts per million of ferrous ion increases the rate many times.
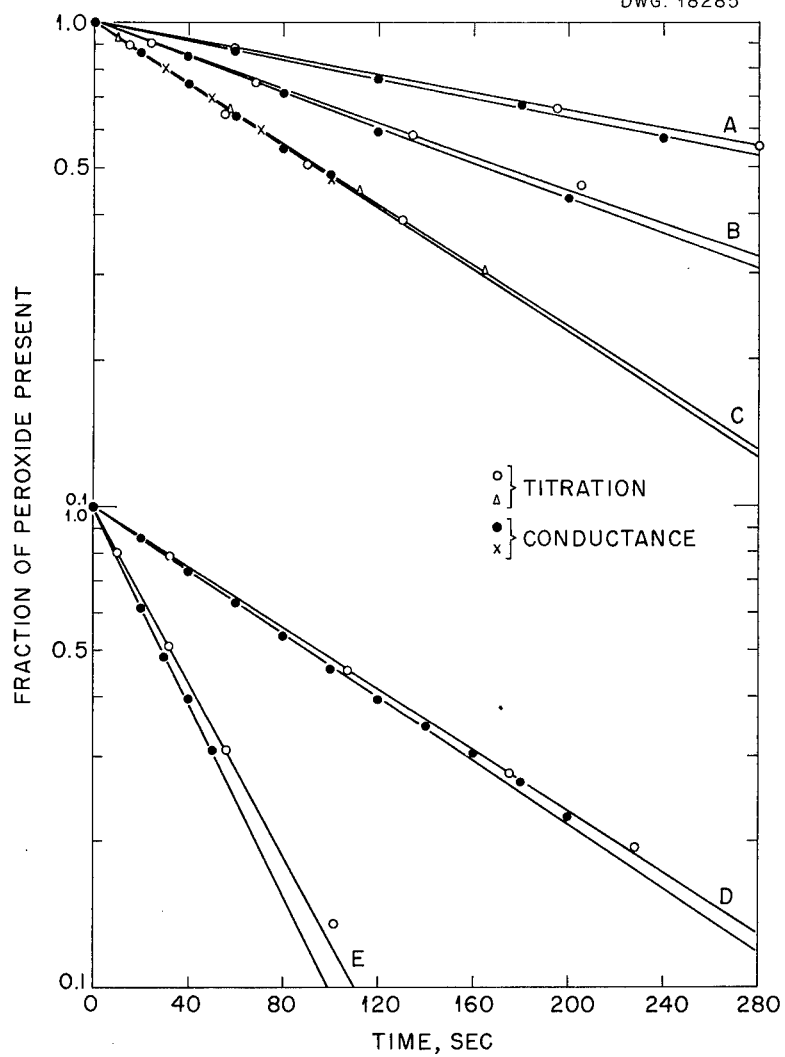
Fig. 11. Correlation of Chemical and Conductance Methods.
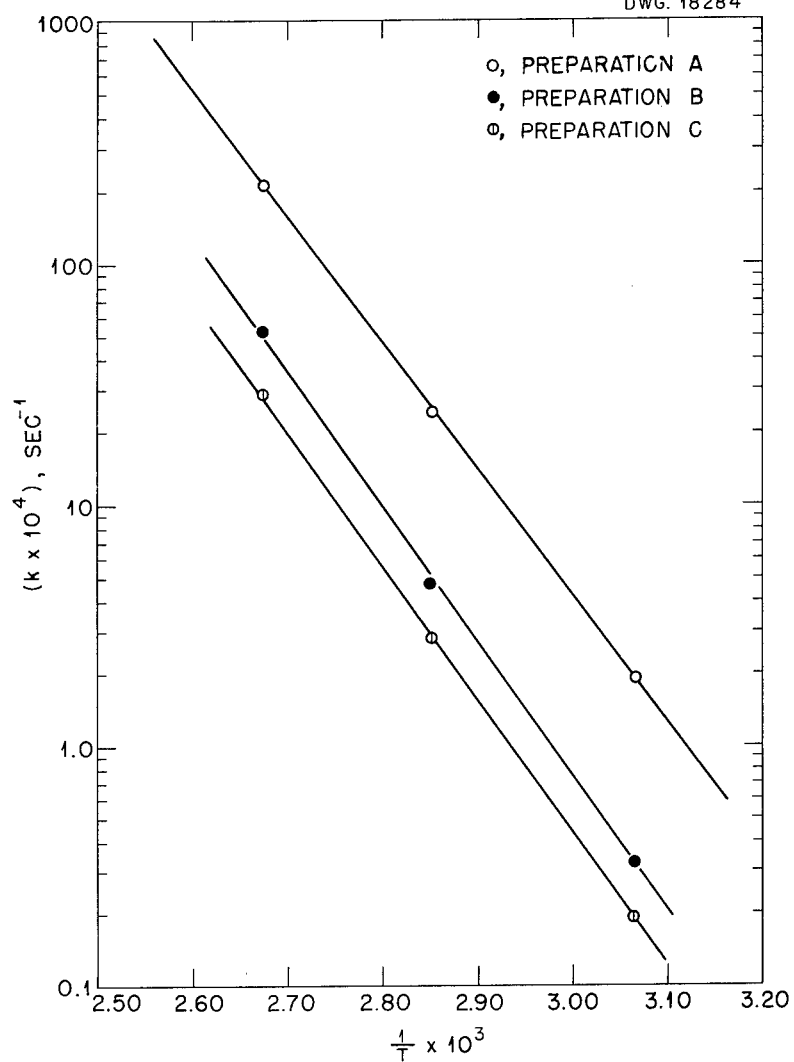
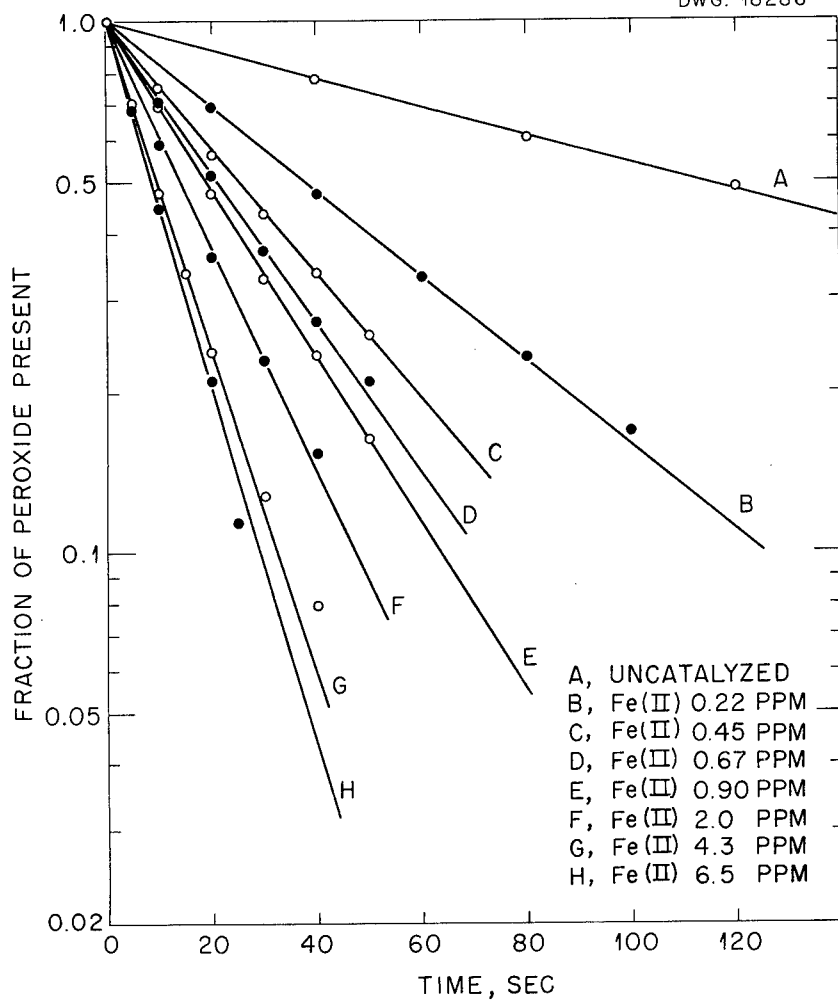Fig. 12.   Peroxide Decomposition as a Function of Temperature.

Fig. 13. Catalytic Effect of Iron on Peroxide Decomposition.

For a specific solution at a specific temperature the decomposition rate can be expressed by the equation,

$$\frac{dC}{dt} = - k\ C \qquad (4)$$

in which C is the total peroxide concentration in moles per liter at time, t, and k is the molar rate constant in the reciprocal of convenient time units, e.g., minutes. In the case of continuous production of peroxide, as in an operating reactor, the equation becomes,

$$\frac{dC}{dt} = \underset{\substack{\text{(Production} \\ \text{rate} \quad) -}}{K} - \underset{\substack{\text{(Decomposition} \\ \text{rate} \quad)}}{k\ C} \qquad (5)$$

In the steady state $\frac{dC}{dt}$ becomes zero and

$$K = k\ C_{ss} \qquad (6)$$

The production rate, K, in moles per liter per minute can be expressed in terms of the yield, G, in molecules per 100 electron volts and the average power density of the reactor, P.D., in kilowatts per liter, by the equation,

$$K = 0.0052\ G \times P.D. \qquad (7)$$

Substituting in equation (6), one obtains,

$$P.D. = \frac{k\ C_{ss}}{0.0052\ G} \qquad (8)$$

In order to avoid precipitation of uranyl peroxide in a reactor, C_{ss} must not be allowed to exceed the solubility of uranyl peroxide. Thus if one knows the decomposition rate constant, the solubility of uranyl peroxide, and the G value at a specific temperature, the maximum safe power level for the reactor at that temperature may be readily calculated. Because of the very great effect of traces of impurities on the value of k, this quantity should be experimentally determined on a sample of the actual reactor solution.

The effect of released gas, hydrogen plus a stoichiometric amount of oxygen from the peroxide decomposition, on the safety of homogeneous reactor operation has long been a matter of concern. The hazards were thought to be

two-fold. First, a sudden collapse of the gas bubbles and the accompanying
sudden density increase might introduce an uncontrollable amount of excess re-
activity. The operation of the Homogeneous Reactor Experiment at Oak Ridge has
proven this a groundless fear insofar as operation at a power density comparable
to the HRE is concerned. The large negative temperature coefficient of the
density smoothed out steady power operation so that only very minor ripples in
reactivity could be observed.

The second possible hazard was the chance that explosions of accumulated
hydrogen-oxygen mixtures might occur with possible damage to the reactor system.
In the HRE this possibility was avoided by diluting the gas mixture with steam.
The gas mixture was then bled to low pressure and, after condensing out the
diluent steam, the hydrogen and oxygen were recombined in a hydrogen burner
followed by a catalyst bed. Future engineering development will undoubtedly
provide a means of controlled recombination of the gases at the pressure of
the reactor.

The criteria which form the basis for a comparison of the relative merits
of several aqueous homogeneous fuel systems have been presented. All of the
systems discussed appear feasible for a comparatively low power reactor operated
at 100°C or less. All have certain objectionable features for high power,
high temperature operation. These have been pointed out. Only uranyl nitrate,
in the Los Alamos Water Boiler, and uranyl sulfate, in the Oak Ridge Homogeneous
Reactor Experiment and in the North Carolina State University Reactor, have
been demonstrated by actual use in a reactor.

Included are the results of contributions by J. W. Boyle, J. S. Gill, E. V.
Jones, F. J. Loprest, H. F. McDuffie, H. A. Mahlman, W. L. Marshall, C. H.
Secoy, M. D. Silverman, G. M. Watson, and H. W. Wright, all of Oak Ridge
National Laboratory.

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